Year: 2018

Bonding of composite resins to PEEK: the influence of adhesive systems and air-abrasion parameters

Stawarczyk, Bogna ; Taufall, Simon ; Roos, Malgorzata ; Schmidlin, Patrick R ; Lümkemann, Nina

Abstract: OBJECTIVE The objective of the study was to investigate the tensile bond strength (TBS) to polyaryletheretherketone (PEEK) after different pretreatment and conditioning methods. METHODS Four hundred PEEK specimens were fabricated and allocated to the following air-abrasion methods (n 1 = 80/pretreatment): (i) 50 m Al2O3 (0.05 MPa); (ii) 50 m Al2O3 (0.35 MPa); (iii) 110 m Al2O3 (0.05 MPa); (iv) 110 m Al2O3 (0.35 MPa); and (v) Rocatec 110 m (0.28 MPa). These pretreatments were combined with the following conditioning methods (n 2 = 20/pretreatment/conditioning): (a) visio.link (VL); (b) Monobond Plus/Heliobond (MH); (c) Scotchbond Universal (SU); and (d) dialog bonding fluid (DB). After veneering of all specimens with dialog occlusal and aging (28 days H2O, 37 °C + 20,000 thermal cycles, 5/55 °C), TBS was measured. Data was analysed using Kaplan-Meier survival analysis with Breslow-Gehan test and Cox-regressions. RESULTS The major impact on TBS showed the conditioning, followed by the air-abrasion-pressure, while the grain size of the air-abrasion powder did not show any effect. Specimens air-abraded at 0.35 MPa showed the highest survival rates. However, within VL groups, this observation was not statistically significant. Within MH groups, pretreatment using 110 m Al2O3 and 0.05 MPa resulted in higher survival rates compared to groups treated with 50 and 110 m Al2O3 using a pressure of 0.35 MPa. The use of VL showed the highest survival rates between the adhesive systems and the TBS values higher than 25 MPa independent of the pretreatment method. As an exception, only VL showed significantly higher survival rates when compared to MH. CONCLUSIONS The adequate choice of the adhesive system and higher pressures improved the TBS between PEEK and veneering resin composite. The particle size had no major impact. CLINICAL RELEVANCE According to this study, best veneering of PEEK with dialog occlusal can be achieved by conditioning with visio.link in combination with the pretreatment of airborne particle abrasion at a pressure of 0.35 MPa.

DOI: https://doi.org/10.1007/s00784-017-2151-x

Originally published at:
Stawarczyk, Bogna; Taufall, Simon; Roos, Malgorzata; Schmidlin, Patrick R; Lümkemann, Nina (2018). Bonding of composite resins to PEEK: the influence of adhesive systems and air-abrasion parameters. Clinical Oral Investigations, 22(2):763-771.
DOI: https://doi.org/10.1007/s00784-017-2151-x

Bonding to PEEK: Influence of air-abrasion parameters and the choice of adhesive systems

Bogna Stawarczyk[1], Simon Taufall[1], Malgorzata Roos[2], Patrick R. Schmidlin[3], Nina Lümkenmann[1]

Short title: Bonding to PEEK

Authors` affiliations

[1]Department of Prosthodontics, Dental School, Ludwig-Maximilians-University Munich, Goethestrasse 70, 80336 Munich, Germany

[2]Department of Biostatistics, Epidemiology, Biostatistics and Prevention Institute, University of Zurich, Hirschengraben 84, 8001 Zurich, Switzerland

[3]Clinic of Preventive Dentistry, Periodontology and Cariology, Center of Dental Medicine, University of Zurich, Switzerland

Keyword: tensile bond strenghs, failure type, PEEK, veneering resin composite, airborne particle abration

Corresponding Author details:

PD Dr. Dipl.-Ing. (FH) Bogna Stawarczyk, MSc

Department of Prosthodontics, Dental School, Ludwig-Maximilians-University Munich, Goethestrasse 70, 80336 Munich, GERMANY

Tel.: +49 89 4400 59573

Fax: +49 89 4400 59502

Email: Bogna.stawarczyk@med.uni-muenchen.de

ABSTRACT

Objective To investigate the tensile bond strength (TBS) to PEEK after different pre-treatment and conditioning methods. *Methods* Four-hundred PEEK specimens were fabricated and allocated to the following air-abrasion methods (n_1=80/pre-treatment): i. 50 µm Al_2O_3 (0.05 MPa); ii. 50 µm Al_2O_3 (0.35 MPa); iii. 110 µm Al_2O_3 (0.05 MPa); iv. 110 µm Al_2O_3 (0.35 MPa); and v. Rocatec 110 µm (0.28 MPa). These pre-treatments were combined with the following conditioning methods (n_2=20/pre-treatment/conditioning): a. visio.link (VL); b. Monobond Plus/Heliobond (MH); c. Scotchbond Universal (SU), d. dialog bonding fluid (DB). After veneering of all specimens with dialog occlusal and aging (28 d H_2O, 37°C+20,000 TC, 5/55°C), TBS was measured. Data was analyzed using Kaplan–Meier survival analysis with Breslow–Gehan-test and Cox-regressions. *Results* The major impact on TBS showed the conditioning, followed by the air-abrasion-pressure, while the grain size of the air-abrasion powder did not show any effect. Significant deviations were found in the frequency of prefailure specimens within the subgroups. Specimens air-abraded at 0.35 MPa showed the highest survival rates. However, within VL groups, this observation was not statistically significant. Within MH groups, pre-treatment using 110 µm Al_2O_3 and 0.05 MPa resulted in higher survival rates compared to groups treated with 50 µm and 110 µm Al_2O_3, with 0.35 MPa pressure. The use of VL showed the highest survival rates between the adhesive systems. Among the specimens treated with 0.35 MPa, VL can be classified within the same range compared to the other adhesive systems. As an exception, only VL showed significantly higher survival rates when compared to MH. However this was not the case in comparsion to SU and DB. *Conclusions* The adequate choice of the adhesive system and higher pressures improved the TBS between PEEK and veneering resin composite. The particle size had no major impact. *Clinical relevance* According to this study, reliable veneering of PEEK with dialogue occlusal can be achieved by conditioning with visio.link in combination with the pre-treatment of airborne particle abrasion at a pressure of 0.35 MPa.

INTRODUCTION

There is a a great interest and ongoing research with regard to substitute materials, which show similar mechanical characteristics like human bone. Metal is one of the materials which is already substituted by polyaryletherketones (PAEK). This substitute material is already used within industrial applications and generally characterized by their high mass-based stability, strong resistance against temperature loads, chemical and physical stress as well as corrosion [1]. The materials, which are currently mainly used in medicine are polyaryletherketoneetherketoneketone (PEKEKK), polyetherketoneketone (PEKK) and polyaryletheretherketone (PEEK) [2]. These materials are additionally characterized by high stabilities against chemical and radiological stresses, where especially PEEK is known for outstanding mechanical properties. PEEK is a high temperature polymer and semi-crystalline thermoplastic, that consists of an aromatic ring with functional groups interconnected by ketones of the previously named group of PAEKs [3, 4, 5]. Due to the outstanding properties in combination with its outstanding biocompatibility and the high stability similar to human bone, the material is used in a variety of applications in the medical field such as spine implants or bone substitute for large defects where autologous bone excretes [7, 8].

Due to the characteristics mentioned above PEEK became very interesting for applications in dentistry as well. The types of applications in dentistry are also manifold but primarily PEEK is used for the fixed dental prosthetic framework (FDP) or the removable partial denture abutment framework [9]. The fact, that the material shows excellent milling and grinding properties [6] is advantageous with respect to the possibility of enlarging the field of indications for PEEK and underlines the potential of the material in dentistry. Previous studies have already shown that PEEK is well processable by Computer Aided Design/Computer Aided Manufacturing (CAD/CAM), because lower deformations and higher fracture loads can be achieved compared to other processes [10]. Besides to all these positve aspects, however, it has to be mentioned that the material has an unaesthetic grey color and appears opaque. Therefore, an additional veneering, at least in the visible area, is indispensable to overcome this rather unaesthetical drawback.

For that reason, various studies have been carried out to investigate the bond strength between PEEK frameworks and resin composites depending on different pre-treatments [5,6,11-18]. In these studies, the pre-treatments had been performed by the use of airborne particle abrasion, treating the surface with piranha-etching [13, 14, 15, 16], sulfuric acid [5, 6, 12, 17] or different types of plasma [18, 19]. Moreover, different adhesive systems for a surface conditioning after pre-treatment have been studied in detail [11,14-16,20,21]. Based on these studies, airborne-particle abrasion could be recommended as one of the best initial pre-treatment options of PEEK surfaces. However, it is striking that in particular the adjustable and varying parameters of this process such as blasting pressure as well as the powder particle grain size of the blasting material have not been studied in detail yet. Moreover, the effect of different adhesive systems as a subsequent treatment and conditioning step after air-abrasion is of big interest, as the chemical mechanism is still questionable in order to achieve a durable bonding.

Therefore, this study was focusing on the influence between five different types of pre-treatments in terms of airborne-particle abrasion with varying pressure and particle sizes in combination with four different adhesive systems on the tensile bond strength (TBS) values between PEEK and veneering material. The null hypothesis of this study was that neither the pre-treatment (particle grain size and pressure) nor the type of adhesive system nor the combination of both has an influence on the TBS between PEEK and the used veneering resin composite.

MATERIALS AND METHODS

In order to perform the TBS tests, a blinded operator cut 400 specimens with a square crosscut of 10x10x3 mm out of PEEK blanks (Tizian PEEK, Schütz Dental, Rosbach, Germany).

PEEK specimens were embedded in a self-cured acrylic resin (ScandiQuick, ScanDia, Hagen, Germany) and grinded with silicone carbide papers (SIC) up to P500 (Tegramin-20, Struers, Ballerup, Danemark). Subsequently, the polished specimens were randomly divided into 20 randomized combinations between pre-treatment and conditioning of the PEEK surface (Figure 1). All used materials are presented in Table 1. Specimens were air-abraded at a distance of 10 mm (basic Quattro IS; Renfert, Hilzingen, Germany) in an angle of 45 ° between the nozzle and the specimen surface. The silica coated groups were air-abraded at an angle of 90 °. Immediately after air-abrasion, the conditioning was performed using different adhesive systems, which are depicted in Figure 2 and described in Table 1. Acrylic cylinders with an inner diameter of 2.9 mm and a length of 10 mm were filled with veneering resin composite (dialogue occlusal, Schütz Dental) and polymerized for 360 s in a laborytory curing devision bre.Lux PowerUnit (intensity: 220 mW/cm², bredent, Senden, Germany). All specimens were stored in distilled water for 28 days at 37 °C and then thermocycled (thermocycler THE 1100; SD mechatronics, Feldkirchen-Westerham, Germany) between 5 °C to 55 °C with a dwell time of 20 s for 20,000 cycles.

TBS measurement was carried out in a standardized machine (Zwick 1445; Zwick, Ulm, Germany). The polymerized acrylic cylinder was fixed into the holding device of the testing machine (Figure 3) and pulled with a crosshead speed of 5 mm/min until the adhesive bond failed. TBS was calculated according to the following equation: s=F/A (s: tensile bond strength [MPa], F: load at fracture [N], A: adhesive area [mm²]). The failure types were analyzed under a stereomicroscope with 50" magnification (Carl Zeiss Axioskop 2 MAT, Zeiss Mikroskopie, Göttingen, Germany) after debonding and classified as follows: (i) adhesive between PEEK substrate and veneering resin composite; (ii) cohesive in the veneering resin composite; and (iii) cohesive in PEEK substrate.

In general, the specimens were divided into sessions in order to guarantee identical conditions for each production session. In each session, 80 specimens were produced, respectively, i.e. 4 specimens per subgroup, since each pre-treatment was combined with each conditioning method.

The measured data was coded in Excel 2010 (Microsoft Corporation; Redmond, WA, USA) and analyzed statistically with SPSS Version 23.0 (IBM, SPSS, Statistics, Armonk, New York, U.S.). Specimens, which showed debonding during thermal cycling and did not survive the aging processes were assigned a TBS value equal to 0 MPa and acted as prefailures. Descriptive statistics such as mean, standard deviation (SD) and 95% confidence intervals were computed. For quantitative variables, the assumption of normality was tested with the Kolmogorov-Smirnov test. The general linear model analysis was performed. Unfortunately, inclusion of prefailures in the analysis can underestimate the true TBS. An alternative approach for statistical analysis is to treat the TBS values for prefailured specimens as censored and actually measured TBS values as non-censored observations. In this setting the Kaplan–Meier survival estimates, Breslow–Gehan tests and the Cox-regressions for the TBS of non-censored and censored data were computed. The results of statistical analyses with p-values less than 0.05 were interpreted as statistically significant.

RESULTS

The descriptive statistics are summarized in Table 2 and visualized via bar graphs in Figure 4. The highest influence on the TBS was exerted by the use of an adhesive system (partial eta squared $\eta_P^2 = 0.510$, $p<0.001$) followed by the pressure during the air-abrasion ($\eta_P^2 = 0.306$, $p<0.001$), while the grain size of the air-abrasion powder did not show a significant effect ($p=0.072$). The effect of the binary, ternary, or quaternary combinations of the three parameters was also significant for the combinations: adhesive system coupled with grain size ($\eta_P^2 = 0.043$, $p=0.001$), adhesive system coupled with pressure ($\eta_P^2 = 0.225$, $p<0.001$), and adhesive system coupled with grain size and coupled with pressure ($\eta_P^2 = 0.028$, $p=0.017$).

Kolmogorov-Smirnov indicated that the data were not normally distributed because the tests were significant for 11 of 20 (55%) subgroups ($\alpha=0.05$). In addition, many subgroups showed prefailured specimens during the aging process (Table 3). Also, significant differences were found in the frequency of prefailured specimens ($p<0.001$, chi-square test). Therefore, the prefailured specimens, which occured during the aging with thermal cycling, were treated as censored and the actually measured TBS values as non-censored observations. Table 4 reports the median survival TBS given by Kaplan–Meier survival observed in different test groups (Figure 5). In summary, the lowest survivel rates were observed for MH.

Impact of pre-treatment

Within VL groups, no statistical impact of pre-treatment on the survival was observed ($p=0.093$). Within SU and DB groups, air-abraded specimens with a pressure of 0.35 MPa showed significantly higher survival rates as compared to specimens, which were treated at 0.05 MPa. The same could be observed for specimens, which were treated with silica-modified corundum particles, regardless of the Al_2O_3 mean particle size (SU and DB: $p<0.001$). Within MH groups, pre-treatment using 110 µm Al_2O_3 and a pressure of 0.35 MPa resulted in higher survival rates compared to groups treated by using 50 µm and 110 µm Al_2O_3, with 0.05 MPa pressure ($p=0.002$).

Impact of adhesive system

Within specimens treated with 50 µm and 110 µm Al_2O_3 and a pressure of 0.05 MPa as well as specimens coated silica-modified corundum particles, VL showed the highest survival rates compared to the remaining adhesive systems ($p<0.001$). Within specimens treated with 50 µm Al_2O_3 and 0.35 MPa pressure VL ranged within the same values as the other adhesive systems ($p=0.06$-0.463). Within 110 µm and 0.35 MPa, VL showed significantly higher survival rates than MH ($p=0.15$). No differences were observed between VL and SU ($p=0.711$) as well as DB ($p=0.718$).

Fracture types

All specimens showed adhesive fractures.

DISSCUSION

The research focus of bonding properties between framework and veneering materials using different pre-treatments and conditioning methods is increasing, especially when it comes to new materials such as PEEK. Previous studies showed that an increase of the surface area achieved by airbone-particle abrasion and the the use of MMA-containing adhesive systems leads to to the improvement of the bonding characteristics of PEEK [11,14, 15,16, 20]. To the best of our knowledge, the influence of the individual parameters of the air-abrasion process (particle grain size and pressure) have not been studied in PEEK materials yet. That is why this study focused on the influence between the pre-treatment with varying parameters such as particle size and applied pressure in combination with the use of different adhesive systems.

In general, the use of PEEK in dentistry as a framework material for FDPs requires a permanently stable and durable bonding to veneering materials. Based on the achieved results, the hypothesis of this study had to be rejected. In summary, the present study showed that the adhesive systems and the pressure during the air-abrasion strongly affected the bonding properties between PEEK and veneering resin composite. In contrast, the grain size of the air-abrasion powder did not show an effect on the bonding characteristics. It was also observed that adhesive systems such as Scotchbond Universal and dialog bonding fluid achieved very good bonding properties by increasing the pressure, while the use of lower pressure resulted in lower values of TBS, respectively. In this case, the values were comparable to those of the well-investigated adhesive system visio.link. In the present study, visio.link acted as the positive control group, because all previous studies showed very high bonding properties after the use of visio.link as conditioner on different pre-treated PEEK surfaces [11,14,15,16]. Also, the survival rates of groups conditioned using visio.link showed the most favourable results so far.

The adhesive systems visio.link and dialog bonding fluid both contain methyl-methacrylate (MMA) monomer, while visio.link contains pentaerythritol-triacrylate (PETIA) as well. In contrast to this, dialoge bonding fluid contains urethane dimethacrylate (UDMA). When looking at the composition of these two adhesive systems, it can be sugested that the component PETIA has a high capacity to modify the PEEK surface, also because visio.link consequently provided even higher bonding properties to PEEK restorations.

Scotchbond Universal is an universal adhesive, which was originally and in theory developed for all restoration materials. It contains 10-Methacryloyloxydecyl-dihydrogenphosphat (MDP) monomer as well as silane and further dimethacrylate in a one bottle approach. In contrast, Monobond Plus and Heliobond represents a two step adhesive system. Monobond Plus is a silane coupling agent with phosphoric acid methacrylate and sulphide methacrylate. Phosphoric acid methacrylate shows good bonding to oxide ceramic and sulphide methacrylate to alloys. However, in this study, the tested PEEK material was unfilled. This may be the reason why no elements were available to which the Monobond Plus was able to chemically dock to. The associated Heliobond has the task to create a bonding between the silane coupling agent Monobond Plus and the composite (in this study veneering resin composite). It contains dimethacrylate, such as bisphenol-A diglycidyl ether dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA). Since Scotchbond Universal (1-bottle system) leads to higher bonding properties, it can be assumed that the 2-bottle system may be prone to errors. It is also conceivable that the immediate contact of the PEEK surface with the dimethacrylate increases the bonding properties. By the use of Monobond Plus/Heliobond adhesive system the PEEK surface is first confronted with the silane coupling agent. Moreover, it is also conceivable that Scotchbond Universal contains other substances, that are on the one hand not named by the manufacturer and on the other hand not known yet to promote the connection to air-abraded PEEK surfaces.

During the experiments of this study it was detected that the PEEK surface properties were changed within a few minutes after performing the pre-treatment by air-abrasion. A longer waiting period after the air-abrasion process resulted in lower TBS values than for specimens which had been veneered immediately after pre-treatment. Therefore, the study was stopped and all specimens were air-abraded, conditioned and veneered immediately. Referring this to the results, the first conclusion, which can be drawn is that an immediate and continous workflow – regarding to the steps of pre-treatment, conditioning and veneerin is one important aspect, which should be considered in order to achieve good bonding properties to any air-abraded PEEK surface. Moreover, this recommodation can be expanded by the fact that PEEK frameworks should be air-abraded with a high pressure.

In general, several test methods can be used to describe the bond properties including the well-known shear bond tests and tensile bond strength tests, or even newer and more accurate test methods, such as micro-shear and micro-tensile tests [22]. Both micro-methods resulted in higher bond strength values due to the smaller bonding area, but at the same time, these methods are very technique-sensitive and elaborate in comparison to the macro test methods [23,24]. However, macro test methods are more commonly used [23,24]. Therefore, macro bond strength test was applied due to their direct and quick results being achieved, as well as their ease of handling [24]. In this study, the used macro tensile test resulted in adhesive failure types of specimens only, after measurements. Therefore, we can state that only the bond strength was measured. The mechanical internal properties of the veneering resin composite are not included in the TBS values. In contrast, shear bond tests often show cohesive failure types and therefore it is supposed that not only the bond strength but more the overall stability is measured using this method.
Regarding to the design of this study, it has to be pointed out that the manufacturing of the specimens was based on the clinical process in order to achieve the transferability of the results to the clinical field, which had not been taken into consideration in previous studies. Due to the manual preparation of PEEK, specimens showed a realistic statistical scattering.

By manually clamping the specimens in the sample holder, small variations may have occured with regard to the pulling direction during the tests. These were estimated to be within the range of 3°, resulting in a negligible systematic error of 0.13%. In order to simulate the clinical situation, thermal cycling as aging procedure was used. Thermal cycling is generally used to imitate the commonly changing temperatures in the oral environment. These thermal changes may induce a reduction of bond strength [25]. In contrast, other studies showed an increase of bonding properties after aging, claiming that it supports the post-polymerization process [26]. Due to the undetermined formal estimation of the quantity of intraoral temperature changes, an arbitrary reference of 10,000 thermal cycles represents one service year [27]. In this study, the specimens were thermally cycled for 20,000 cycles. This corresponds to approximately 2 years. In summary, the results of this study therefore represent clinically relevant results. However, a clinical trial with a controlled standardized study design should evaluate the clinical long-term performance as well.

CONCLUSIONS

Within the limitations of the present study, the following conclusions can be drawn:

- The adhesive systems must be carefully chosen based on their composition.
- Visio.link as an adhesive system for PEEK is user-friendly. Hence, in combination with the investigated variation of air-abrasion parameters no impact on the bonding propertied could be observed
- The conditioning using VL showed the highest survival rates compared to the remaining adhesive systems.
- After air-abrasion with pressure of 0.35 MPa Scotchbond Universal and dialog bonding fluid could achieve TBS values compared to the values using visio.link.
- Monobond Plus with Heliobond showed the lowest TBS values and the lowest survival rates.
- Specimens air-abraded with 0.35 MPa showed the highest survival rates.
- The grain size of the air-abrasion powder particle did not show an effect on TBS.

ACKNOWLEDGMENTS

The authors would like to thank Schütz Dental, bredent and Ivoclar Vivadent for material support of this study.

COMPLIANCE WITH ETHICAL STANDARDS

All procedures performed in studies involving human participants are in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki Declaration and its later amendments or comparable ethical standards.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

FUNDING

This study received no funding.

ETHICAL APPROVAL

This article does not contain any studies with human participants or animals performed by any of the authors.

INFORMED CONSENT

For this type of study, formal consent is not required.

REFERENCES

[1] Salamone, JC. Polymeric materials encyclopedia 4, CRC Press 1996

[2] Ebnesajjad S. Handbook of Polymer Applications in Medicine and Medical Devices. William Andrew Publishing 2013.

[3] Kurtz SM, Devine JN (2007) PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials 28:4845-69.

[4] Toth JM, Wang M, Estes BT, Scifert JL, Seim HB 3rd, Turner AS (2006) Polyetheretherketone as a biomaterial for spinal applications. Biomaterials 27:324-34.

[5] Stawarczyk B, Beuer F, Wimmer T, Jahn D, Sener B, Roos M, et al. (2013) Polyetheretherketone - a suitable material for fixed dental prostheses? J Biomed Mater Res B Appl Biomater 101:1209-16.

[6] Schmidlin PR, Stawarczyk B, Wieland M, Attin T, Hammerle CH, Fischer J (2010) Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. Dent Mater 26:553-9.

[7] Klingler JH, Krüger MT, Sircar R, Kogias E, Scholz C, Volz F, Scheiwe C, Hubbe U, et al. (2014) PEEK cages versus PMMA spacers in anterior cervical discectomy: comparison of fusion, subsidence, sagittal alignment, and clinical outcome with a minimum 1-year follow-up. Scientific World Journal 398-6.

[8] O'Reilly EB, Barnett S, Madden C, Welch B, Mickey B, Rozen S, et al. (2015) Computed-tomography modeled polyether ether ketone (PEEK) implants in revision cranioplasty. J Plast Reconstr Aesthet Surg 68(3):329-38.

[9] Schwitalla A, Muller WD (2013) PEEK dental implants: a review of the literature. J Oral Implantol 39:743-9.

[10] Stawarczyk B, Eichberger M, Uhrenbacher J, Wimmer T, Edelhoff D, Schmidlin PR (2015) Three-unit reinforced polyetheretherketone composite FDPs: influence of fabrication method on load-bearing capacity and failure types. Dent Mater J 34:7-12.

[11] Stawarczyk B, Keul C, Beuer F, Roos M, Schmidlin PR (2013) Tensile bodn strength of veneering resins to PEEK: Imapct of different adhesives. Dent Mater J 32:441-8.

[12] Sproesser O, Schmidlin PR, Uhrenbacher J, Eichberger M, Roos M, Stawarczyk B (2014) Work of adhesion between resin composite cement and PEEK as a function of etching duration with sulfuric acid and ist correlation with bond strength values. Int J Adhesion Adhesives 54:184-90.

[13] Hallmann L, Mehl A, Senero N, Hämmerle CHF (2012) The improvement of adhesive properties of PEEK through pretreatments. Appl Surface Sci 258:7213-8.

[14] Keul C, Liebermann A, Schmidlin PR, Roos M, Sener B, Stawarczyk B (2014) Influence of PEEK surface modification on surface properties and bond strength to veneering resin composites. J Adhes Dent 16:383-92.

[15] Stawarczyk B, Jordan P, Schmidlin PR, Roos M, Eichberger M, Gernet W, et al. (2014) PEEK surface treatment effects on tensile bond strength to veneering resins. J Prosthet Dent 112:1278-88.

[16] Uhrenbacher J, Schmidlin PR, Keul C, Eichberger M, Roos M, Gernet W, et al. (2015) The effect of surface modification on the retention strength of

polyetheretherketone crowns adhesively bonded to dentin abutments. J Prosthet Dent 112:1489-97.
[17] Sproesser O, Schmidlin PR, Uhrenbacher J, Roos M, Gernet W, Stawarczyk B (2014) Effect of sulfuric acid etching of polyetheretherketone on the shear bond strength to resin cements. J Adhes Dent 16:465-72.
[18] Stawarczyk B, Bahr N, Beuer F, Wimmer T, Eichberger M, Gernet W, et al. (2014) Influence of plasma pretreatment on shear bond strength of selfadhesive resin cements to polyetheretherketone. Clin Oral Investig 18:163-70.
[19] Ourahmoune R, Salvia M, Mathia TG, Mesrati N (2014) Surface morphology and wettability of sandblasted PEEK and its composites. Scanning 36:64-75.
[20] Kern M, Lehmann F (2012) Influence of surface conditioning on bonding to polyetheretherketon (PEEK). Dent Mater 28:1280-3.
[21] Rosentritt M, Preis V, Behr M, Sereno N, Kolbeck C (2015) Shear bond strength between veneering composite and PEEK after different surface modifications. Clin Oral Investig 19(3):739-44.
[22] Andrade AM, Moura SK, Reis A, Loguercio AD, Garcia EJ, Grande RHM (2010) Evaluating resin-enamel bonds by microshear and microtensile bond strength tests: effect of composite resin. J Appl Oral Sci 18:591-8.
[23] Heintze SD, Zimmerli B (2011) Relevance of *in vitro* tests of adhesive and composite dental materials. Schweiz Monatsschr Zahnmed 121:1024-40.
[24] Eren D, Bektas ÖÖ, Siso SH (2013) Three different adhesive systems; three different bond strength test methods. Acta Odontol Scan 71:978-83.
[25] Torstenson B, Brannström M (1988) Contraction gap under composite resin restorations: effect of hygroscopic expansion and thermal stress. Oper Dent 13:24-31.
[26] Bähr N, Keul C, Edelhoff D, Eichberger M, Roos M, Gernet W, Stawarczyk B (2013) Effect of different adhesives combined with two resin composite cements on shear bond strength to polymeric CAD/CAM materials. Dent Mater J 32:492-501.
[27] Gale MS, Darvell BW (1999) Thermal cycling procedures for laboratory testing of dental restorations. J Dent 27:89-99.

Figures and Tables

Figure 1. Study design: overview of all tested groups.

Figure 2. Used adhesive systems for conditioning of PEEK specimens.

Figure 3. Holding device for TBS measurement with a specimen.

Figure 4. Bar graph for tested TBS (mean ± SD) of all subgroups.

Figure 5. Cumulative distribution fuction for prefailured specimens with respect of TBS [MPa] by Kaplan – Meier.

Table 1: Summary of used products, compositions, manufacturers and the application steps.

Table 2: Overview of descriptive statistics included mean, standard devidation (SD) and 95% confidence interval (95%CI) for tensile bons strength values divided into the different pretreatment and preconditioning. All values are listed in MPa.

Table 3. Relative frequency with 95% confidence interval (95%CI) of debonded (prefailured) specimens before TBS measurement. All values are listed in %.

Table 4. Median survival TBS and 95% confidence interval (95%CI) of survival in all subgroups. All values are listed in MPa.

Figure 1. Study design: overview of all tested groups.

Substrate	preconditioning	Ashesive system	composite
PEEK (Tizian PEEK) 10mm x 10mm x 3mm (N=400)	⍰ = 50 µm , pressure = 0.05 MPa (n=80)	VL (n=20)	dialog occlusal (N=400)
		SU (n=20)	
		MH (n=20)	
		DB (n=20)	
	⍰ = 50 µm , pressure = 0.35 MPa (n=80)	VL (n=20)	
		SU (n=20)	
		MH (n=20)	
		DB (n=20)	
	⍰ = 110 µm , pressure = 0.05 Mpa (n=80)	VL (n=20)	
		SU (n=20)	
		MH (n=20)	
		DB (n=20)	
	⍰ = 110 µm , pressure = 0.35 MPa (n=80)	VL (n=20)	
		SU (n=20)	
		MH (n=20)	
		DB (n=20)	
	rocatec method; ⍰ = 110 µm, pressure = 0.28 (n=80)	VL (n=20)	
		SU (n=20)	
		MH (n=20)	
		DB (n=20)	

Figure 2. Used adhesive systems for conditioning of PEEK specimens.

Figure 3. Holding device for TBS measurement with a specimen.

Figure 4. Bar graph for tested TBS (mean ± SD) of all subgroups.

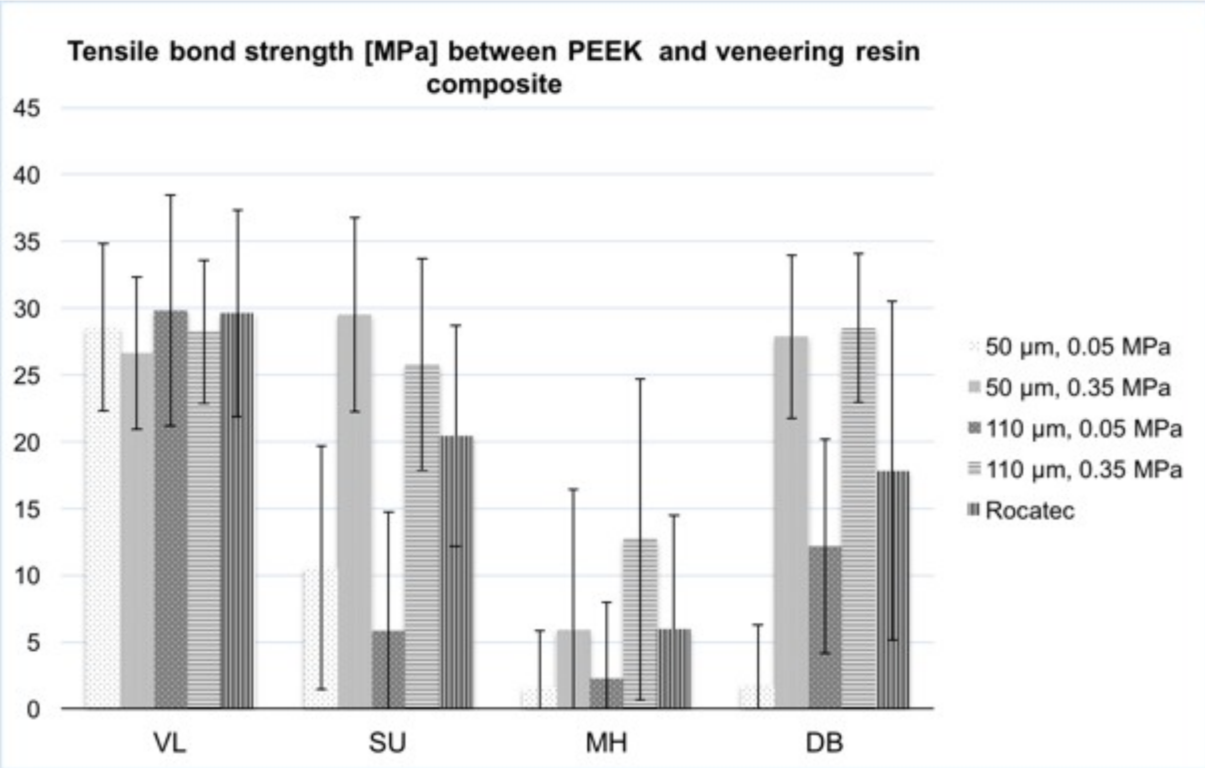

Figure 5. Cumulative survival function for prefailured and non-prefailured specimens with respect of TBS [MPa] by Kaplan – Meier. A: VL, B: SU, C: MH, and D: DB.

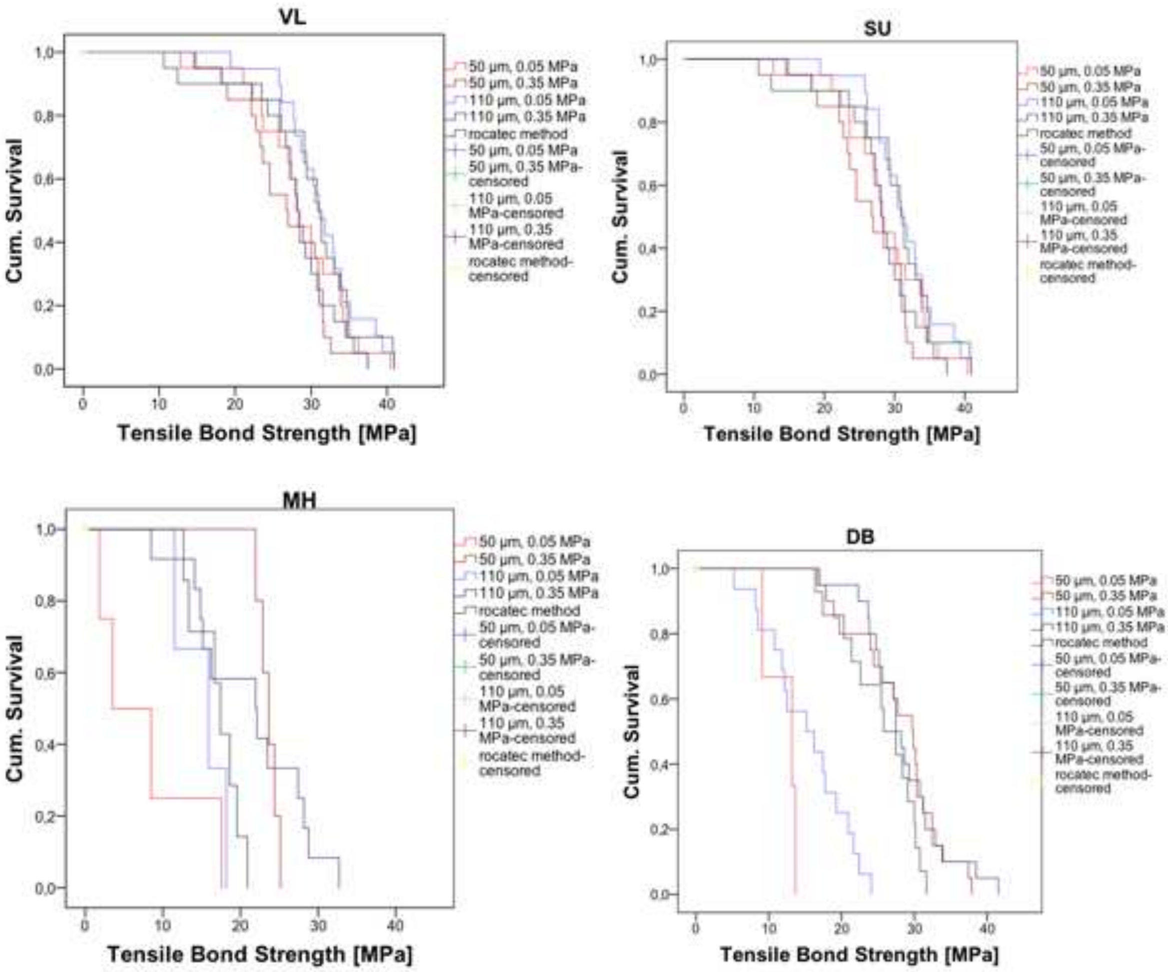

Table 1: Summary of used products, compositions, manufacturers and the application steps.

Material	Product Name	Abbreviation	Manufacturer	Application steps as recommended by the manufacturer	Composition	Lot No.	Curing light used
Adhesives	visio.link	VL	bredent, Senden, Germany	1. Apply adhesive on the PEEK surface with a brush 2. Light cure for 90 s (bre.Lux PowerUnit, intensity: 220 mW/cm², bredent, Senden, Germany)	MMA, PETIA, Photoinitiators	114784	bre.Lux PowerUnit, intensity: 220 mW/cm², bredent, Senden, Germany
	Scotchbond Universal	SU	3M ESPE, Seefeld, Germany	1. Apply with disposable applicator and rub it in for 20 s 2. Subsequently direct a gentle stream of air over the liquid for about 5 s Light cure for 10 s	MDP Phosphate Monomer, DM, HEMA, Vitrebond Copolymer, Filler, Ethanol, Water, Silane	521215	Elipar Freelight 2, 1200 mW/cm²,3M, Seefeld, Germany
	Monobond Plus	MH	Ivoclar Vivadent, Schaan, Liechtenstein	1. Apply with a microbrush for 60 s 2. Disperse dry remaining excess with a strong stream of air	Silane methacrylate, phosphoric acid methacrylate, sulphide methacrylate	S14727	-
	Heliobond			1. Apply it for 15-30 s 2. Carefully rinse with water and dry with a	Bis-GMA, TEGDMA	R22281	Elipar Freelight 2, 1200 mW/cm²,3M,

	Fluid		Rosbach, Germany				intensity: 220 mW/cm², bredent, Senden, Germany
Veneering composite	Dialog Occlusal			Light cure for 360 s	UDMA, Bis-GMA, 1,4-butane dioldomethacrylate	2014009689	

Abbreviations: MMA, methyl methacrylate; Bis-GMA, bisphenol-A diglycidyl ether dimethacrylate; TEGDMA, Triethyleneglycol dimethacrylate; UDMA, Urethane dimethacrylate; HEMA, Hydroxyethylmethacrylate; DM, dimethacrylate; MDP, 10-Methacryloyloxydecyl-dihydrogenphosphat

Table 2: Overview of descriptive statistics included mean, standard devidation (SD) and 95% confidence interval (95%CI) for tensile bons strength values divided into the different pretreatment and preconditioning. All values are listed in MPa.

Pretreatment Pretreatment	VL		SU		MH		DB	
	Mean (SD)	95% CI	Mean (SD)	95% CI	Mean (SD)	95% CI	Mean (SD)	95% CI
Al_2O_3 50 µm 0.5 bar	28.58 (6.27)	[25.6;31.6]	10.58 (9.09)*	[6.3;14.9]	1.57 (4.28)*	[-0.5;3.6]	1.80 (4.46)*	[-0.3;3.9]
Al_2O_3 50 µm 3.5 bar	26.61 (5.69)	[23.9;29.3]	29.52 (52.9)	[26.1;33.0]	5.90 (10.50)*	[0.9;10.9]	27.86 (6.12)	[24.9;30.8]
Al_2O_3 110 µm 0.5 bar	29.82 (8.64)*	[25.7;33.9]	5.83 (79.49)*	[1.6;10.0]	2.28 (5.68)*	[-0.4;5.0]	12.20 (8.01)	[8.4;16.0]
Al_2O_3 110 µm 3.5 bar	28.24 (5.36)	[25.7;30.8]	25.76 (7.92)	[22.0;29.5]	12.68 (12.01)*	[7.0;18.3]	28.52 (5.59)	[25.8;31.2]
Rocatec	29.61 (7.72)*	[25.9;33.3]	20.44 (8.28)	[16.5;24.4]	5.96 (8.51)*	[1.9;10.0]	17.83 (12.69)*	[11.8;23.8]

*not normally distributed groups

Table 3. Relative frequency with 95% confidence interval (95%CI) of debonded (prefailured) specimens before TBS measurement. All values are listed in %.

Pretreatment	VL		SU		MH		DB	
	rel. frequancy	95% CI	rel. frequancy	95% CI	rel. frequancy	95% CI	rel. frequancy	95% CI
Al_2O_3 50 µm 0.5 bar	0	[0;17]	20	[4;44]	80	[55;95]	85	[61;97]
Al_2O_3 50 µm 3.5 bar	0	[0;17]	0	[0;17]	75	[49;92]	0	[0;17]
Al_2O_3 110 µm 0.5 bar	5	[0;25]	65	[39,85]	85	[61;97]	20	[4;44]
Al_2O_3 110 µm 3.5 bar	0	[0;17]	0	[0;17]	40	[18;64]	0	[0;17]
Rocatec	0	[0;17]	0	[0;17]	65	[39;85]	75	[49;92]

Table 4. Median survival TBS and 95% confidence interval (95%CI) of survival in all subgroups. All values are listed in MPa.

Pretreatment	VL		SU		MH		DB	
	Median	95% CI	Median	95% CI	Median	95% CI	Median	95% CI
Al_2O_3 50 µm 0.5 bar	28.0	[26.0;29.1]	15.3	[6.5;24.0]	3.6	[0;10.1]	13.2	[6.5;19.8]
Al_2O_3 50 µm 3.5 bar	26.8	[21.3;32.1]	30.9	[20.5;41.3]	23.6	[21.9;25.3]	29.7	[25,0;34.4]
Al_2O_3 110 µm 0.5 bar	31.1	[28.8;33.3]	17.4	[5.1,29.6]	15.9	[8.7;23.0]	15.2	[7.8;22.4]
Al_2O_3 110 µm 3.5 bar	28.2	[27.0;29.2]	26.4	[23.8;28.9]	22.0	[11.8;32.1]	27.4	[25.7;29.0]
Rocatec	30.9	[29.9;31.8]	20.0	[13.2;26.7]	17.4	[15.3;19.4]	25.8	[22.0;29.4]